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SISUNINE, A GLYCOALKALOID FOUND IN HYBRIDS BETWEEN *SOLANUM ACAULE* AND *SOLANUM* × *AJANHUIRI*

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Key Word Index—*Solanum acaule*; *Solanum ajanhuiri*; hybrids; glycoalkaloids; sisunine.

Abstract—Clones of hybrids of *Solanum acaule* and *Solanum* × *ajanhuiri* contain two glycoalkaloids, the previously identified commersonine and an unknown glycoalkaloid, sisunine, which is considered to be the tomatidine O(3)-β-commertetraoside.

INTRODUCTION

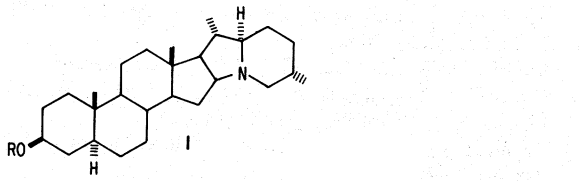
The diversity of glycoalkaloids found in *Solanum* species [1] is, in part, the result of the independent inheritance of the aglycone and glycosidic moieties [2]. This inheritance pattern can be helpful in determining parents of a particular hybrid. Such is the case for a group of clones referred to as sisu which are cultivated by the Aymara people in the 'altiplano' of Western Bolivia. These clones are believed to be hybrids between *Solanum acaule* × *Solanum* × *ajanhuiri* [3]. The wild parent of *S.* × *ajanhuiri* (*S. megistacrolobum*) contains glycoalkaloids that have the demissidine aglycone (**1**) and the commertetraose saccharide unit (**3**) [3]; *S. acaule* contains the glycoalkaloids demissine, which is composed of the aglycone demissidine and the tetrasaccharide lycotetraose (a terminal glucose in **3** replaced by xylose), and tomatine [tomatidine (**2**) as aglycone, lycotetraose as saccharide moiety] [4]. The sisu hybrids would be expected to contain a glycoalkaloid that has tomatidine as aglycone (from *S. acaule*) and commertetraose as saccharide moiety (from *S.* × *ajanhuiri*). In this communication we report the glycoalkaloid composition of the sisu hybrid and the characterization of a new glycoalkaloid which results from the independent inheritance of aglycone and saccharide.

RESULTS

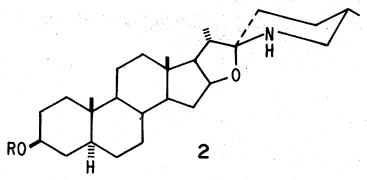
All the 'sisu' clones contained two major ammonia precipitable components as determined by TLC. One of these compounds was readily identified as commersonine by comparison of its TLC behavior, GC/MS of the aglycone and GC analysis of the monosaccharides with an authentic sample of commersonine. The unknown glycoalkaloid named sisunine, yielded on hydrolysis tomatidine (determined by GC/MS) and the sugars galactose and glucose (determined by GC of aldononitrile derivatives). The fast atom bombardment mass spectrum (FAB-MS) (Table 1) confirms the M_r of sisunine to be 1063 and has a fragmentation pattern which is consistent with the sequential loss of four hexoses from a tomatidine aglycone [5] as shown in structure **3**. Permethylation analysis indicated hexoses with three different substitution patterns: unsubstituted, 4-substituted and 2,3-disubstituted which is again consistent with the structure **3**. According to these results, sisunine is considered to be the tomatidine O(3)-β-commertetraoside.

EXPERIMENTAL

For FAB-MS the sample was added to glycerol on the probe with 1 μl N oxalic acid. GC/MS were obtained using a 20 m OV-



1



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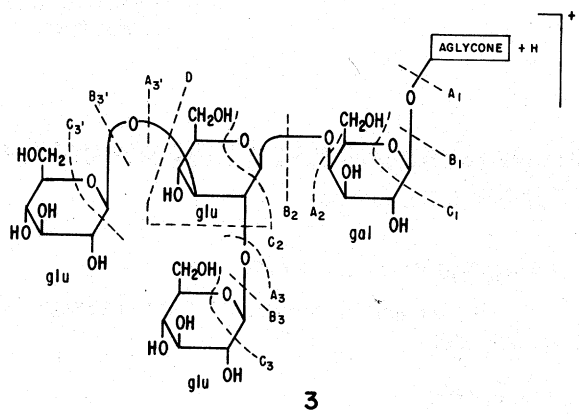

3

Table 1. FAB mass spectrum of sisunine

M/z	Rel. int.	Fragmentation
1064	100	MH^+
930	14	C_3 or C_3^1
902	10	
901	4	B_3 or B_3^1
900	6	
886	8	
885	6	A_3 or A_3^1
884	12	
706	12	D
606	18	C_2
578	22	
577	8	B_2
576	16	
562	14	
561	10	A_2
560	26	
445	20	C_1
444	60	
416	54	
415	16	B_1
414	46	
399	34	
398	94	A_1
397	16	
396	32	

101 capillary column. Silica gel G plates (250 μm) were used for TLC.

Glycoalkaloids were extracted from tubers with 5% MeOH–HOAc and ppted from 0.1 N H_2SO_4 with conc. NH_4OH; the total amount of glycoalkaloid isolated was 20 mg. The individual glycoalkaloids were purified by prep. TLC using the lower layer of MeOH–$CHCl_3$ (1:1) satd with 0.5 parts 1% NH_4OH; sisunine ran slightly ahead of demissine. Sugars were determined by GC of the corresponding aldononitrile derivatives [6] and the position of substitution in the sugars was determined by the modified Hakamori permethylation procedure [7].

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